

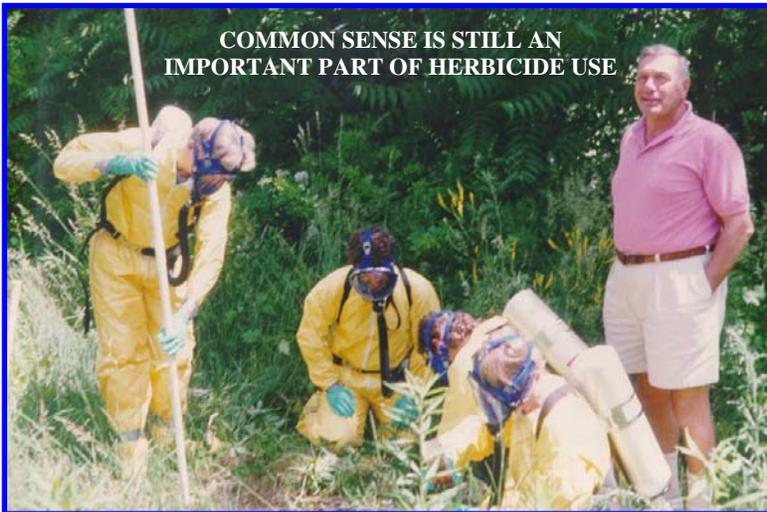
# LINCOLN COUNTY NOXIOUS WEED CONTROL

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## Website

[http://www.co.lincoln.wa.us/WeedBoard/  
default.htm](http://www.co.lincoln.wa.us/WeedBoard/default.htm)

COMMON SENSE IS STILL AN  
IMPORTANT PART OF HERBICIDE USE



Credits: Weed Control Methods Handbook: Tools & Techniques for Use in Natural Areas. Mandy Tu, Callie Hurd & John M. Randall. The Nature Conservancy Wildland Invasive Species Team. Version April 2001

LINCOLN COUNTY  
NOXIOUS WEED CONTROL

# Herbicide FACTS

## *Separating Fact from Fiction*



## WHAT'S INSIDE?

- Understand what it is you are using
- Get a better understanding about what herbicides do
- Learn what impact they have on our animals and environment
- How you can use them in your management plan

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	Category III	Category IV
g	>500-5000 mg/kg	>5000 mg/kg
/kg	>2000-5000 mg/kg	>5000 mg/kg
/liter	>2000-5000 mg/liter	>5000 mg/liter
ement or irrita- 18-20 days	Corneal involvement or irrita- tion clearing in < 7 days	Minimal effects clearing < 24 hrs
n > 72 hrs	Moderate irritation > 72 hrs	Mild or slight irritation
	<b>CAUTION</b>	<b>CAUTION</b>

- Manufacturer, Registration and Establishment Numbers** – The name and address on the label should be used for contacting the product manufacturer. The Registration number is the EPA number that identifies the registered product. The Establishment number identifies where the product was produced.
- Warranty** – The warranty statement is not required but often is provided by the manufacturer.

Always read  
the label before  
applying  
herbicides

Study	Category I	Category II
Acute Oral	$\geq 50$ mg/kg	>50-500 mg/kg
Acute Dermal	$\geq 200$ mg/kg	>200-2000 mg
Acute Inhalation	$\geq 0.05$ mg/liter	>200-2000 mg
Eye Irritation	Corrosive or corneal involvement or irritation persisting >20 days	Corneal involvement clearing in
Skin Irritation	Corrosive	Severe irritation
Signal Word	<b>DANGER</b>	<b>WARNING</b>

7. **Signal Word** – The signal word indicates how dangerous or toxic a product can be. The signal words “**danger**”, “**warning**”, or “**caution**” is determined by a combination of acute toxicity studies, and the toxicity of each of the product components. Each toxicity study is assigned a toxicity category, and the highest category determines the signal word that appears on the label. Additionally, “**poison**” and the skull-crossbones symbol are required for products in toxicity category I for acute oral, dermal, or inhalation exposure, or for products that contain certain “**inerts**”.
8. **Statement of Practical Treatment** – This section highlights important first aid information for treating people exposed to the product.

Herbicides belong to a group of chemicals known as pesticides, which prevent, destroy, repel, or mitigate any pest. Herbicides are any chemical substance that is used to specifically kill plants. Other familiar pesticides are insecticides, rodenticides, and fungicides.

### MODE OF ACTION

An herbicide’s **mode of action** is the biochemical or physical mechanism by which it kills plants. Most herbicides kill plants by disrupting or altering one or more of their metabolic processes. Some species or whole groups or plants are not susceptible to certain herbicides because they use different biochemical pathways or have slightly different enzymes. Animals typically suffer **little or no effect** from most herbicides sold today because these compounds principally affect processes **exclusive to plants**, like photosynthesis or production of aliphatic amino acids.



### **HERBICIDE FAMILIES VS. MODE OF ACTION**

Herbicides that are chemically similar are said to belong to the same “**herbicide family**”. The compounds in a given family typically exhibit similar characteristics and function, due to their chemical and structural similarities. For example, clopyralid, picloram, and triclopyr are all grouped in the pyridine family.

An herbicide’s **mode of action** is the mechanism (biochemical or physical) by which it kills or suppresses plants. The mode of action is generally dictated by its chemical structure, and therefore, herbicides in the same family, tend to have the same Mode of Action. For instance, clopyralid, picloram, and triclopyr are all in the pyridine family and are all auxin mimic herbicides, while glyphosate is an amino acid inhibitor. Some herbicides from different families, however, can have the same mode of action. For example, the phenoxy 2,4-D is an auxin mimic, just like the pyridines picloram, clopyralid, and triclopyr.

The Herbicide Table on page 28 of this handbook indicates the family and mode of action for each herbicide covered in this manual.

A good supplement to this booklet is “**PNW 437—Herbicide-Resistant Weeds and Their Management**” bulletin. This publication contains the **Herbicide Rotation reference poster**.

6. **Brand Name, Chemical or Trade Name, Common Name, Formulation, Ingredients, & Contents** – The **brand name** is the name chosen by the manufacturer for marketing purposes. Often the same herbicide formulation is marketed for different uses under different brand names. For example, triclopyr amine is sold as Garlon 3A<sup>®</sup> for commercial use, but a slightly different formulation is sold as Turflon Ester<sup>®</sup> for residential use. The **chemical name** describes the molecular formula of the active ingredient. Examples of chemical names include: 3,6-dichloro-pyridinecarboxylic acid for clopyralid, or N-(phosphonomethyl) glycine for glyphosate. The **common chemical name** is for the active ingredient itself - it is not specific to the formulation. Examples of common chemical names include glyphosate and triclopyr.

Pesticides are marketed in a variety of **formulations** including emulsifiable concentrates, wettable powders, and soluble powders. Often the brand name indicates the formulation type. For example, Garlon 3A<sup>®</sup> is the amine formulation of triclopyr.

The product **ingredients** are listed as the percentage of active and “inert” ingredients in the product. The active ingredient is the pesticidally active chemical. Unlike most commonly accepted definitions of “inert”, the inert ingredients in a pesticide product include all ingredients that are not pesticidally active. This does not necessarily imply that these ingredients are non-toxic, non-flammable, or otherwise non-reactive. The **contents** describe the total product weight or liquid volume in the package.

3. **Reentry Statement** – This section identifies the period of time following treatment when re-entry to the treated area is prohibited. If no statement is given, re-entry should not be attempted until the spray dries or the dust settles. Check with the county agricultural commissioner for local restrictions.
4. **Storage and Disposal Directions** – This section outlines appropriate storage and disposal procedures for unused portions of the pesticide and of the pesticide container.
5. **Statement of Use Classification** – Each pesticide is designated and prominently labeled as “**General Use**” or “**Restricted Use**”. “**Restricted use**” pesticides are those that would pose a significant threat to the applicator or the environment without further regulatory restrictions. Only certified pesticide applicators may apply “**restricted use**” pesticides, and additional safety precautions may be required. The status of each pesticide can be found in the **U.S. EPA’s Restricted Use Products list** (<http://www.epa.gov/RestProd/rupoct00.htm>). Of the herbicides listed in this handbook, only **picloram** is of “**restricted use**.” Be sure to check for additional state restrictions (for example, certain container sizes of 2,4-D are of “restricted use”).

### Herbicides attack plants

An herbicide is often chosen for use based on its mode of action. If one herbicide is ineffective, another herbicide with a different mode of action may provide better results. When and how an herbicide is applied may be determined by its mode of action. **Pre-emergent** herbicides are those applied to the soil before the weed germinates, and either disrupt germination or kill the germinating seedling. **Post-emergent** herbicides are those that are applied directly to already established plants and/or soil. Some herbicides are effective both before (**pre-emergent**) and after (**post-emergent**) germination.

Some of the most common modes of action include:

- **Auxin mimics** (2,4-D, clopyralid, picloram, and dicamba), which mimic the plant growth hormone auxin, causing uncontrolled and disorganized growth in susceptible plant species;
- **Mitosis inhibitors** (fosamine), which prevent re-budding in spring and new growth in summer (also known as dormancy enforcers);
- **Photosynthesis inhibitors** (hexazinone), which block specific reactions in photosynthesis leading to cell breakdown;
- **Amino acid synthesis inhibitors** (glyphosate, metsulfuron and chlorsulfuron, which prevent the synthesis of amino acids required for construction of proteins;
- **Lipid biosynthesis inhibitors** (fluzifop-p-butyl and sethoxydim), that prevent the synthesis of lipids required for growth and maintenance of cell membranes.

## Auxin Mimics

Picloram, clopyralid, triclopyr, and 2,4-D are referred to as synthetic auxins. **Auxin** is a plant hormone that regulates growth in many plant tissues. Chemically, 2,4-D is classified as a phenoxy acetic acid, while picloram, clopyralid, and triclopyr are pyridine derivatives. When susceptible plants are treated with these herbicides, they exhibit symptoms that could be called 'auxin overdose', and eventually die as a result of increased rates of disorganized and uncontrolled growth.

In use since 1945, 2,4-D is one of the most studied herbicides in the world. It is known to affect many biochemical processes in plants, but it is still not clear which of the biochemical alterations 2,4-D and other auxin-



mimic herbicides cause that is ultimately responsible for killing plants. It is possible that plants are weakened more or less equally by several of these disruptions with no one process being the most important.

Mode of Action determines the effectiveness of the herbicide you are using

## Product Label

HERBICIDE

2

Directions for Use (continued)

son]

CROP/SITE \_\_\_\_\_

ified Applicators or  
and only for those  
tor's certification.

CROP/SITE \_\_\_\_\_

CROP/SITE \_\_\_\_\_

NAME

CROP/SITE \_\_\_\_\_

XX.00%

CROP/SITE \_\_\_\_\_

0.00%

CROP/SITE \_\_\_\_\_

0.00%

CROP/SITE \_\_\_\_\_

of \_\_\_ per gallon.

CROP/SITE \_\_\_\_\_

OF CHILDREN

ison]

nes]

10

WARRANTY STATEMENT

DITIONAL PRE-  
ITS

gistrant Name]  
dress, City,  
e, zip code]

Sample Pro

1	<p>PRECAUTIONARY STATEMENTS</p> <p>HAZARD TO HUMANS AND DOMESTIC ANIMALS (Signal Word) _____ _____ _____</p> <p>ENVIRONMENTAL HAZARDS _____ _____ _____</p> <p>PHYSICAL OR CHEMICAL HAZARDS _____ _____ _____</p> <p>DIRECTIONS FOR USE: It is a violation of Federal law to use this product in a manner inconsistent with its labeling.</p>	5	<p>RESTRICTED USE P</p> <p>Due to: [insert rea</p> <p>For retail sale to and use only by Cert persons under their direct supervision uses covered by the Certified Applica</p>
2	<p>RESTRICTED USE PESTICIDE</p>	6	<p>PRODUCT M</p> <p>ACTIVE INGREDIENT(S):</p> <p>INERT INGREDIENTS: XX</p> <p>TOTAL: 100</p> <p>This product contains ___ lbs</p>
3	<p>RE-ENTRY STATEMENT (if applicable)</p>	7	<p>KEEP OUT OF REACH C</p> <p>Signal Word [Pe</p> <p>[Skull &amp; Crossbor</p> <p>First Aid</p>
4	<p>STORAGE AND DISPOSAL</p> <p>STORAGE _____ _____</p> <p>DISPOSAL _____ _____</p>	8	<p>SEE SIDE PANEL FOR ADI CAUTIONARY STATEMEN</p> <p>EPA Registration No. _____ [Re</p> <p>EPA Establishment No. _____ [Ad</p> <p>Stat</p>
		9	<p>Net Contents _____</p>

Grasses and other monocots are generally not susceptible to auxin-mimic herbicides. The reason for this selectivity is unclear because there are no apparent differences between the binding sites targeted by auxins in monocots and dicots. It may, however, be due to differences in vascular tissue structure or differences in ability to translocate or metabolize the herbicide (DiTomaso 1999).

### Amino Acid Synthesis Inhibitors

Glyphosate and metsulfuron kill plants by preventing the synthesis of certain amino acids produced by plants but not animals. Glyphosate blocks the action of the enzyme 5-enolpyruvylshikimate-3-phosphate (EPSP) synthase, which inhibits the biosynthesis of certain aromatic amino acids such as phenylalanine, tyrosine, and tryptophan. These amino acids are required for protein synthesis, which, in turn, is necessary for plant growth and maintenance. Other biochemical processes such as carbohydrate translocation, can also be affected by these herbicides. Although these effects are considered secondary, they may be important in the total lethal action of glyphosate.



## FORMULATIONS

An **herbicide formulation** is the total marketed product, and is typically available in forms that can be sprayed on as liquids or applied as dry solids. It includes the active ingredient(s), any additives that enhance herbicide effectiveness, stability, or ease of application such as surfactants and other adjuvants, and any other ingredients including solvents, carriers, or dyes. The application method and species to be treated will determine which formulation is best to use. In most cases, manufacturers produce formulations that make applications and handling simpler and safer. Some herbicides are available in forms that can reduce risk of exposure during mixing, such as pre-measured packets that dissolve in water, or as a liquid form already mixed with surfactant and dye (e.g., Pathfinder II<sup>®</sup>).



**Formulations are available in liquids or dry solids**

All chemical manufacturers must provide a MSDS to employers purchasing the chemicals. The product label and MSDS should both be included with any product. Both documents contain important and reliable information that should be thoroughly reviewed before the product is used.

### Label Contents

1. **Precautionary Statements** – Pesticide labels highlight three types of hazards associated with use of the product. The “**hazards to people and domestic animals**” section explains if and why a pesticide is hazardous, its potential adverse effects, and safety gear that applicators are required to wear. The “**environmental hazards**” section discusses potential environmental damage including impacts to non-target organisms, such as fish and wildlife, and provides measures that can minimize ecological impacts. The “**physical and chemical hazards**” section outlines potential hazards due to the chemical and physical nature of the product, such as flammability and explosiveness.
2. **Directions for Use** – The directions outline where, when, and how much of a pesticide may be used and any special restrictions. For herbicides, it lists all plants or types of plants that the formulation in question is registered to control. **The law requires compliance with these directions.** An herbicide may not be used to control a species or type of plant that is not listed on its label.

## HOW TO READ AN HERBICIDE LABEL

All pesticides registered for use in the U.S. must have a label that has been approved by the federal Environmental Protection Agency (EPA). The label contains information about the product, including its relative toxicity, potential hazard to humans and the environment, directions for use, storage and disposal, and first aid treatment in case of exposure. Product labels are legal documents whose language is determined and approved by the EPA during the pesticide registration process. Any use of a pesticide inconsistent with the label requirements is prohibited by law.

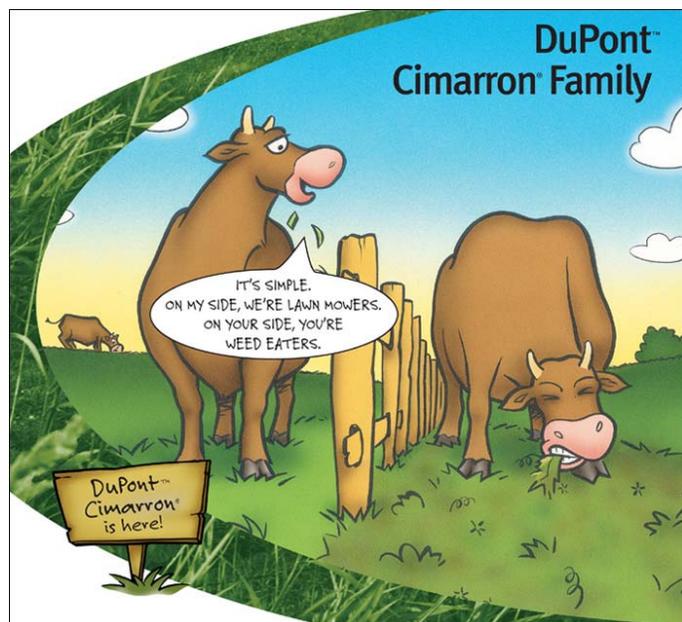
Labels contain very specific information in language that is tightly regulated by the US EPA. The word “**must**” is used for actions that are required by law, while the word “**should**” is used for actions that are recommended but not required. One of the “**Signal words**” (caution, warning, danger, and poison) used by the EPA to indicate relative toxicity to humans, must appear on each label (see below).

**Material Safety Data Sheets (MSDSs)** are similar to product labels but need not contain the same information. While product labels are regulated and required by the EPA, MSDSs are required by the U.S. Occupational Safety and Health Administration (OSHA) for the protection of employees using pesticides or other hazardous chemicals.

## Sprayable/liquid formulations include:

1. **Water-soluble formulations:** soluble liquids (SL), soluble powders or packets (SP), and soluble granules (SG). Only a few herbicidal active ingredients readily dissolve in water. These products will not settle out or separate when mixed with water.
2. **Emulsifiable formulations (oily liquids):** emulsifiable concentrates (E or EC) and gels (GL). These products tend to be easy to handle and store, require little agitation, and will not settle out of solution. Disadvantages of these products are that most can be easily absorbed through the skin and the solvents they contain can cause the rubber and plastic parts of application equipment to deteriorate.
3. **Liquid suspensions (L for liquid or F for flowable)** that are dispersed in water include: suspension concentrates (SC), aqueous suspensions (AS), emulsions of water-dissolved herbicide in oil (EO), emulsions of an oil-dissolved herbicide in water (EW), micro-encapsulated formulations (ME), and capsule suspensions (CS). All these products consist of a particulate or liquid droplet active ingredient suspended in a liquid. They are easy to handle and apply, and rarely clog nozzles. However, they can require agitation to keep the active ingredients from separating out.

4. Dry solids that are suspended in water: wettable powders (W or WP), water-dispersible granules (WDG, WG, DG), or dry flowables (DF). These formulations are some of the most widely used. The active ingredient is mixed with a fine particulate carrier, such as clay, to maintain suspension in water. These products tend to be inexpensive, easy to store, and are not as readily absorbed through the skin and eyes as ECs or other liquid formulations. These products, however, can be inhalation hazards during pouring and mixing. In addition, they require constant agitation to maintain suspension and they may be abrasive to application



NO ENDORSEMENT OF NAMED PRODUCTS IS INTENDED NOR IS CRITICISM IMPLIED OF SIMILAR PRODUCTS NOT MENTIONED.

Impurities produced during the manufacturing process and adjuvants added to the formulation may be more toxic than the herbicide compound itself. Consequently, LD50s determined for the technical grade of the herbicide may not be the same as that for the brand name formulation. Combinations of herbicides furthermore, can have additive and synergistic effects in which a formulation of two or more herbicides is two to 100 times as toxic as any one of the herbicides alone (Thompson 1996). **Labels should be read carefully for manufacturer's warnings and safety precautions that may be required for a particular formulation**

***NOTE:*** It is important to remember while interpreting study results discussed in this manual and elsewhere that changes in technology have lowered the detectable residue level 1,000-fold over the last twenty years. Herbicide residues that could only be detected to the **parts per million (ppm)** level (e.g. one microgram of pesticide per kilogram of soil) in the early 1970's can now be detected at the **parts per billion (ppb)** level (e.g., one microgram of pesticide per 1,000 kilograms of soil). When a study reports finding no residues it really means that no residues above the lowest detectable level were found. This can be an important difference in comparing the results of studies conducted in the 1960's and 70's to studies from the 1980's and 90's.

Herbicides can poison the body by blocking biochemical processes or dissolving or disrupting cell membranes. Small doses may produce no response while large doses can cause severe illness or death. The effects may be localized, such as irritation to the eyes, nose, or throat, or generalized, such as occurs when the compound is distributed through the body via the blood stream. Symptoms can occur immediately after exposure or develop gradually. Injuries are usually reversible, but in extreme cases can be permanently debilitating (Marer 1988).

Common symptoms of low-level exposure (such as occurs when mixing or applying herbicides in water) to many herbicides include skin and eye irritation, headache, and nausea.

**Injuries are usually reversible, but in extreme cases can be permanently debilitating**

Higher doses (which can occur when handling herbicide concentrates) can cause blurred vision, dizziness, heavy sweating, weakness, stomach pain, vomiting, diarrhea, extreme thirst, and blistered skin, as well as behavioral alterations such as apprehension, restlessness, and anxiety (Marer 1988). Extreme cases may result in convulsions, unconsciousness, paralysis, and death.

### Dry formulations include:

1. **Granules (G)** – Granules consist of the active ingredient absorbed onto coarse particles of clay or other substance, and are most often used in soil applications. These formulations can persist for some time and may need to be incorporated into the soil.
2. **Pellets (P) or tablets (TB)** – Pellets are similar to granules but tend to be more uniform in size and shape.
3. **Dusts (D)** – A dust is a finely ground pesticide combined with an inert or inactive dry carrier. They can pose a drift or inhalation hazard.

**These products can be inhalation hazards**

### Salts vs. Esters

Many herbicidally active compounds are acids that can be formulated as a salt or an ester for application. Once the compound enters the plant, the salt or ester cation is cleaved off allowing the parent acid (active ingredient) to be transported throughout the plant. When choosing between the salt or ester formulation, consider the following characteristics:

**Salts**

- Most salts are highly water soluble, which reduces the need for emulsifiers or agitation to keep the compound suspended.
- Salts are not soluble in oil.
- Salts generally require a surfactant to facilitate penetration through the plant cuticle (waxy covering of leaves and stems).
- Salts are less volatile than esters.
- Salts can dissociate in water. In hard water the parent acid (i.e. the active ingredient) may bind with calcium and magnesium in the water, precipitate out, and be inactivated.

**Esters can penetrate  
plant tissues more  
readily than salts**

**Esters**

- Esters can penetrate plant tissues more readily than salts, especially woody tissue
- Esters generally are more toxic to plants than salts
- Esters are not water soluble and require an emulsifying agent to remain suspended in water-based solvents
- Esters have varying degrees of volatility

Oral LD50 Mammals (Rats)	LD50 - Birds (BW - bobwhite quail, M - mallards)	LC50 - Fish (bluegill sunfish)	Dermal LD50 - Rabbit
764 mg/kg [low]	500 mg/kg (BW) [moderate]	263 mg/L [moderate]	NA
4,300 mg/kg [low]	1,465 mg/kg (M) [low]	125 mg/L [moderate]	>2,000 mg/kg
>4,000 mg/kg	> 5,000 mg/kg (M) > 5,000 mg/kg (BW)	>980 mg/L	NA
757-1,707 mg/kg	2,009 mg/kg (M)	135 mg/L	2,000 mg/kg
5,600 mg/kg [slight]	> 4,640 mg/kg (BW/M) [low]	120 mg/L [moderate]	>5000 mg/kg
> 4,000 mg/kg	>2,510 mg/kg (M)	150 mg/L	>2,000 mg/kg
> 5,000 mg/kg [slight]	> 2,510 mg/kg (M) [low]	>14.4 mg/L [high]	>2000 mg/kg
713 mg/kg [low]	1,698 mg/kg (M) [low]	148 mg/L [moderate]	>2000 mg/kg

Herbicide	Microbial Degradation	Chemical Degredation	Solar Degradation
2,4 D	Primary mechanism	Minor mechanism	Low potential
Clopyralid	Primary mechanism	Minor mechanism	Low potential
Chlorsulfuron	Primary mechanism	Minor mechanism	Low potential
Dicamba	Primary mechanism	Minor mechanism	Low potential
Glyphosate	Primary mechanism	Minor mechanism	Low potential
Metsulfuron	Primary mechanism	Minor mechanism	Low potential
Picloram	Primary mechanism	Primary mechanism	Moderate potential
Triclopyr	Primary mechanism	Minor mechanism	Moderate potential

### Adjuvants (including surfactants)

An **adjuvant** is any material added to a pesticide mixture that facilitates mixing, application, or pesticide efficacy. An adjuvant enables an applicator to customize a formulation to be most effective in a particular situation. Adjuvants include surfactants, stickers, extenders, activators, compatibility agents, buffers and acidifiers, deposition aids, de-foaming agents, thickeners, and dyes.

*Surfactants are adjuvants that facilitate the movement of herbicides into the plant*

### *Surfactants*

**Surfactants** are the most important adjuvants. They are chemical compounds that facilitate the movement of the active herbicide ingredient into the plant. They may contain varying amounts of fatty acids that are capable of binding to two types of surfaces, such as oil and water. Some herbicide formulations come with a surfactant already added, in others, surfactants can be added prior to application. Whether a surfactant should be added will be determined by the type of herbicide being applied and the target plant. **Read the label for recommendations of appropriate surfactants.**

## MECHANISMS OF DISSIPATION

**Dissipation** refers to the movement, degradation, or immobilization of an herbicide in the environment.

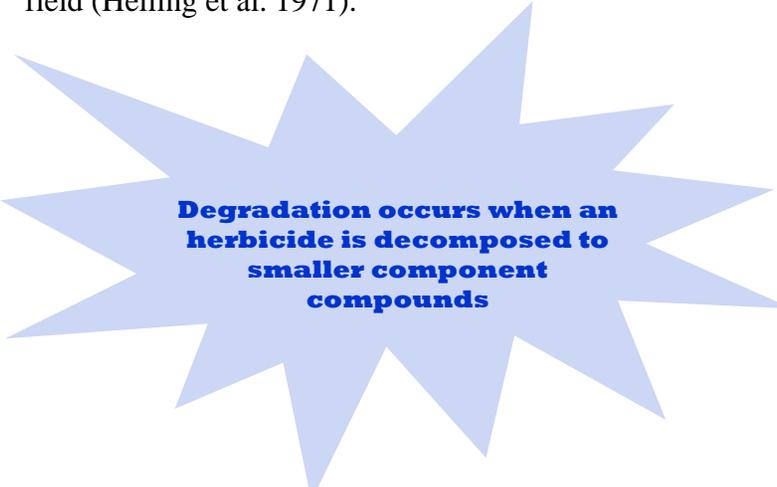
**Degradation** occurs when an herbicide is decomposed to smaller component compounds, and eventually to CO<sub>2</sub>, water, and salts through photochemical, chemical, or biological (microbial metabolism) reactions (Freed and Chiou 1981). Biodegradation accounts for the greatest percentage of degradation for most herbicides (Freed and Chiou 1981). When a single herbicide degrades, it usually yields several compounds (“**metabolites**”), each of which has its own chemical properties including toxicity, adsorption capacity, and resistance to degradation. Some metabolites are more toxic and/or persistent than the parent compound. In most cases, the nature of the metabolites are largely unknown.



Mobility in Soil	Water Solubility	Average Half-life in Water
moderate-high	900 mg/L (acid), 100 mg/L (ester), 796,000 mg/L (salt)	varies from hours to months
moderate-high	1,000 mg/L (acid), 300,000 mg/L (salt)	8-40 days
high	28,296 mg/l	1,230 days
Very high	28,895 mg/l	30 days
low	15,700 mg/L (acid), 900,000 mg/L (IPA salt), 4,300,000 mg/L	12 days to 10 weeks
high	9,500 mg/l	35.8 days
moderate-high	430 mg/L (acid), 200,000 (salts)	2-3 days
moderate-high	430 mg/L (acid), 23 mg/L (ester), 2,100,000 mg/L (salt)	4 days

Herbicide	Average Soil Half-life	Soil Sorption (Koc)
2,4 D	10 days	20 mL/g (acid/salt), 100 mL/g (ester)
Clopyralid	40 days	avg 6 mL/g but ranges to 60 mL/g
Chlorsulfuron	40	40ml/g
Dicamba	14	2 ml/g
Glyphosate	47 days	24,000 mL/g
Metsulfuron	30	35 ml/g
Picloram	90 days	16 mg/L (can range -17-160 mL/g)
Triclopyr	30 days	20 mL/g (salt), 780 mL/g (ester)

***Photodegradation*** refers to decomposition by sunlight. Sunlight intensity varies with numerous factors including latitude, season, time of day, weather, pollution, and shading by soil, plants, litter, etc. Studies of the photodegradation of herbicides are often conducted using UV light exclusively, but there is some debate as to whether most UV light actually reaches the surface of the earth. Therefore, photodegradation rates determined in the laboratory may over-estimate the importance of this process in the field (Helling et al. 1971).



**Degradation occurs when an herbicide is decomposed to smaller component compounds**

***Microbial Degradation***

**Microbial degradation** is decomposition through microbial metabolism. Different microbes can degrade different herbicides, and consequently, the rate of microbial degradation depends on the microbial community present in a given situation (Voos and Groffman 1997, McCall et al. 1981). Soil conditions that maximize microbial degradation include warmth, moisture, and high organic content.

Herbicides may be microbially degraded via one of two routes. They may be metabolized directly when they serve as a source of carbon and energy (i.e. food) for microorganisms (Hutzinger 1981), or they may be co-metabolized in conjunction with a naturally occurring food source that supports the microbes (Hutzinger 1981). Herbicides that are co-metabolized do not provide enough energy and/or carbon to support the full rate of microbial metabolism on their own.



There is sometimes a lag time before microbial degradation proceeds. This may be because the populations of appropriate microbes or their supplies of necessary enzymes start small, and take time to build-up (Farmer and Aochi 1987, Kearney and Karns 1960). If this lag time is long, other degradation processes may play more important roles in dissipation of the herbicide (Farmer and Aochi 1987). Degradation rates of co-metabolized herbicides tend to remain constant over time.

Herbicide Family	Target Weed Sps.	Mode of Action
phenoxy	broadleaf weeds	Auxin mimic
pyridine	annual and perennial broadleaf weeds	Auxin mimic
sulfonylureas	annual and perennial broadleaf weeds	Amino acid inhibitor
benzoic acid	annual and perennial broadleaf weeds	Auxin mimic
none generally recognized	annual and perennial weeds	Amino acid inhibitor
sulfonylureas	annual and perennial broadleaf weeds	Amino acid inhibitor
pyridine	annual and perennial broadleaf weeds, vines, and woody plants	Auxin mimic
pyridine	woody and annual broadleaf weeds	Auxin mimic

Herbicide	Brand Name Examples	Chemical Name
2,4 D	Navigate <sup>®</sup> , Class <sup>®</sup> , Weed-Pro <sup>®</sup> , Justice <sup>®</sup>	(2,4-dichlorophenoxy) acetic acid
Clopyralid	Reclaim <sup>®</sup> , Curtail <sup>®</sup> , Transline <sup>®</sup>	3,6-dichloro-2- pyridinecarboxylic acid
Chlorsulfuron	Glean <sup>®</sup> , Telar <sup>®</sup>	(2-chloro-N-[ (4-methoxy-6-methyl- 1,3,5-triazin-2-yl) aminocarbonyl ] benzenesulfonamide
Dicamba	Banvel <sup>®</sup> , Clarity <sup>®</sup> ,  Vanquish <sup>®</sup>	3,6-dichloro-O-anisic acid
Glyphosate	RoundUp <sup>®</sup> , Rodeo <sup>®</sup> , Accord <sup>®</sup>	N-(phosphonomethyl)glycine
Metsulfuron	Ally <sup>®</sup> , Escort <sup>®</sup>	Methyl 2-[[[4-methoxy-6-methyl- 1,3,5-triazin-2-yl)amino]carbonyl ] amino]sulfonyl] benzoate
Picloram	TordonK <sup>®</sup>	4-amino-3,5,6-trichloro-2- pyridinecarboxylic acid
Triclopyr	Garlon <sup>®</sup> , Remedy <sup>®</sup>	[(3,5,6-trichloro-2-pyridinyl)oxy] acetic acid

***Chemical Decomposition***

**Chemical decomposition** is degradation driven by chemical reactions, including hydrolyzation (reaction with hydrogen, usually in the form of water), oxidation (reaction with oxygen), and disassociation (loss of an ammonium or other chemical group from the parent molecule). The importance of these chemical reactions for herbicide degradation in the field is not clear (Helling et al. 1971).

**Immobilization/Adsorption**

Herbicides may be immobilized by adsorption to soil particles or uptake by non-susceptible plants. These processes isolate the herbicide and prevent it from moving in the environment, but both adsorption and uptake are reversible. In addition, adsorption can slow or prevent degradation mechanisms that permanently degrade the herbicide.

**Adsorption refers to the binding of herbicide by soil particles, and rates are influenced by characteristics of the soil and of the herbicide.**

Adsorption is often dependent on the soil or water pH, which then determines the chemical structure of the herbicide in the environment. Adsorption generally increases with increasing soil organic content, clay content, and cation exchange capacity, and it decreases with increasing pH and temperature. Soil organic content is thought to be the best determinant of herbicide adsorption rates (Farmer and Aochi 1987, Que Hee and Sutherland 1981, Helling et al. 1971).

Adsorption increases  
with increasing soil  
organic content

Adsorption is also related to the water solubility of an herbicide, with less soluble herbicides being more strongly adsorbed to soil particles (Helling et al. 1971).

Solubility of herbicides in water generally decreases from salt to acid to ester formulations, but there are some exceptions. For example, glyphosate is highly water-soluble and has a strong adsorption capacity.



The availability of an herbicide for transport through the environment or for degradation is determined primarily by the adsorption/desorption process (WHO 1984). Adsorption to soil particles can stop or slow the rate of microbial metabolism significantly. In other cases, adsorption can facilitate chemical or biological degradation (Farmer and Aochi 1987). Adsorption can change with time and, in most cases, is reversible (i.e. the herbicide can desorb from the soil or sediments and return to the soil solution or water column).

*“glyphosate is highly water-soluble and has a strong adsorption capacity”*

Agricultural herbicide applicators are typically exposed to herbicide levels ranging from micrograms to milligrams per cubic meter of air through inhalation, but exposures through the skin are thought to be much greater (Spear 1991). Spilling concentrated herbicide on exposed skin can be the toxic equivalent of working all day in a treated field (Libich et al. 1984). Dermal exposure can occur to the hands (directly or through permeable gloves), splashes onto clothing or exposed skin, and anywhere you wipe your hands (e.g., thighs, brow).



Some tests have found relatively high levels of dermal exposure to the crotch and seat of workers who got herbicide on their hands, and then touched or wiped the seat of their vehicles. Because adsorption through the skin is the most common route of exposure for applicators (Marer 1988), the dermal LD50 may provide more practical information on the relative toxicity of an herbicide rather than the oral LD50, which is based on oral ingestion.

### **Toxic Effects**

A person's reaction to pesticide poisoning depends on the toxicity of the pesticide, the size of the dose, duration of exposure, route of absorption, and the efficiency with which the poison is metabolized and excreted by the person's body (Marer 1988, Ware 1991). Different individuals can have different reactions to the same dose of herbicide. Smaller people are, in general, more sensitive to a given dose than are larger people (Marer 1988).

## HUMAN TOXICOLOGY

When proper safety precautions are taken, human exposure to herbicides used in natural areas should be minimal. Properly fitted personal protection equipment and well-planned emergency response procedures will minimize exposure from normal use as well as emergency spill situations.



### Exposure

Agricultural workers are often exposed to herbicides when they unintentionally re-enter a treated area too soon following treatment. People who mix and apply herbicides are at the greatest risk of exposure. The most common routes of exposure are through the skin (dermal) or by inhalation (to the lungs). Accidental spills or splashing into the eyes is also possible and with some compounds, can result in severe eye damage and even blindness.

## Movement/Volatilization

**Movement** through the environment occurs when herbicides are suspended in surface or subsurface runoff, volatilized during or after application, evaporated from soil and plant surfaces, or leached down into the soil. Although generally studied and discussed separately, these processes actually occur simultaneously and continuously in the environment (Hutzinger 1981).



**Volatilization** occurs as the herbicide passes into the gaseous phase and moves about on the breeze. Volatilization most often occurs during application, but also can occur after the herbicide has been deposited on plants or the soil surface. The volatility of an herbicide is determined primarily by its molecular weight. Most highly volatile herbicides are no

longer used.

Volatility generally increases with increasing temperature and soil moisture, and with decreasing clay and organic matter content (Helling et al. 1971). The use of a surfactant can change the volatility of a herbicide (Que Hee and Sutherland 1981). In extreme cases, losses due to volatilization can be up to 80 or 90% of the total herbicide applied (Taylor and Glotfelty 1988). Of the herbicides described in detail in this handbook, only 2,4-D and triclopyr can present significant volatilization problems in the field (T. Lanini, pers. comm.).

## BEHAVIOR IN THE ENVIRONMENT

Perhaps the most important factor determining the fate of herbicide in the environment is its solubility in water (Hutzinger 1981). Water-soluble herbicides generally have low adsorption capacities, and are consequently more mobile in the environment and more available for microbial metabolism and other degradation processes. Esters, in general, are relatively insoluble in water, adsorb quickly to soils, penetrate plant tissues readily, and are more volatile than salt and acid formulations (Que Hee and Sutherland 1981).

### Soils

An herbicide's is often de-life (also DT50). The it takes for cide applied to pate. The a rough esti-tence of an half-life of a can vary sig-



ing on soil characteristics, weather (especially temperature and soil moisture), and the vegetation at the site. Dissipation rates often change with time (Parker and Doxtader 1983). For example, McCall et al. (1981) found that the rate of dissipation increased until approximately 20% of the applied herbicide remained, and then declines. Nonetheless, half-life values do provide a means of comparing the relative persistence of herbicides.

persistence in soils scribed by its half-known as the half-life is the time half of the herbi-the soil to dissi-half-life gives only mate of the persis-herbicide since the particular herbicide nificantly depend-

For example, loss of invasive riparian plants can cause changes in water temperature and clarity that can potentially impact the entire aquatic community, and the physical structure of the system through bank erosion. Removing a shrubby understory can make a habitat unsuitable for certain bird species and expose small mammals to predation.

### Aquatic Species

An herbicide's toxicity to aquatic organisms is quantified with the LC50, which is the concentration of herbicide in water required to kill half of the study animals. The LC50 is typically measured in micrograms of pesticide per liter of water.

In general, ester formulations are more dangerous for aquatic species than salt and acid formulations because ester formulations are lipophilic (fat-loving), and consequently, can pass through the skin and gills of aquatic species relatively easily. Ester formulations, additionally, are not water soluble, and are less likely to be diluted in aquatic systems.

### Soil Microbes

Herbicides have varying effects on soil microbial populations depending on herbicide concentrations and the microbial species present. Low residue levels can enhance populations while higher levels can cause population declines. In many cases, studies are too short in duration to determine the true long-term impacts of herbicide use on soil microbes.

The lower the LD-50 the more acutely toxic the chemical is.

<u>Chemical Name</u>	<u>LD-50</u>	<u>Half-Life</u>
Gasoline	19	---
Caffeine	190	---
2,4-D	300 to 1,000	7 to 28 days
Aspirin	1240	---
Banvel	1700	5 months
Table Salt	3320	---
Telar/Glean	5545	3 months
Roundup	5600	7.5 days
Tordon	8200	5 months/pint

The LD50 does not provide any information about chronic, long-term toxic effects that may result from exposure to lesser doses. Sublethal doses can lead to skin or eye irritation, headache, nausea, and, in more extreme cases, birth defects, genetic disorders, paralysis, cancer,

*“The LD50 does not provide any information about chronic, long-term effects that may result from exposure to lesser doses.”*

and even death. Impurities derived from the formulation of the herbicide and the adjuvants added to the formulation may be more toxic than the herbicide compound itself, making it difficult to attribute increased risks of cancer or

other effects directly to an herbicide (Ibrahim et al. 1991).

The most dramatic effects of herbicides on non-target plants and animals often result from the habitat alterations they cause by killing the targeted weeds.

The distribution of an herbicide in the soil is determined primarily by the amount, type, and surface area of clays and organic matter in the soil, the amount and quality of soil moisture, and soil temperature and soil pH (Helling et al. 1971). Most natural soils have pH values between 5 and 8 (V. Claassen, pers. comm.). Rainfall and the amount of leaching that has occurred strongly influences these values. In wet areas and/or coarse soils, cations can be leached out, leaving the soil acidic. In arid and semi-arid regions, soils retain cations and are more alkaline. Acidic soils can also be found in bogs where organic acids lower the soil's pH.

### Water

Water bodies can be contaminated by direct overspray, or when herbicides drift, volatilize, leach through soils to groundwater, or are carried in surface or subsurface runoff. Amounts of leaching and runoff are largely dependent on total rainfall the first few days after an application. Total losses to runoff generally do not exceed five to ten percent of the total applied, even following heavy rains (Taylor and Glotfelty 1988). **High soil adsorption capacity, low rates of application, and low rainfall reduce total runoff and contamination of local waterways (Bovey et al. 1978).**



*“Total losses to runoff generally do not exceed five to ten percent of the total applied, even following heavy rains.”*

The behavior of an herbicide in water is dictated by its solubility in water. Salts and acids tend to remain dissolved in water until degraded through photolysis or hydrolysis. Esters will often adsorb to the suspended matter in water, and precipitate to the sediments. Once in the sediments, esters can remain adsorbed to soil particles or be degraded through microbial metabolism. Highly acidic or alkaline waters can chemically alter an herbicide and change its behavior in water. [The average pH of surface waters is between five and nine \(Hutzinger 1981\).](#)



## ENVIRONMENTAL TOXICITY

The toxicology information reported in this handbook is for the technical grade of the herbicide unless otherwise noted. In some cases, it is not the herbicide itself that is the most toxic component of the applied formula. Adjuvants, such as petroleum solvents (e.g. diesel fuel, deodorized kerosene, methanol), can be highly toxic (Ware 1991). In addition, impurities resulting from the manufacturing process can be more toxic than the active ingredient itself.

## Birds and Mammals

An herbicide's toxicity is described by its LD50, which is the dose received either orally (taken through the mouth) or dermally (absorbed through the skin) that kills half the population of study animals. The oral LD50s reported here were determined for adult male rats. The dermal LD50s were determined for rabbits. The LD50 is typically reported in grams of herbicide per kilogram of animal body weight. LD50s are determined under varying circumstances so comparisons between different herbicides may provide only a rough sense of their relative toxicities. Dermal LD50 values may be more meaningful to herbicide applicators because they are more likely to be exposed to herbicide through their skin rather than by oral ingestion. In any event, very few people, even among applicators, are exposed to herbicide doses as high as the LD50.

- Most **herbicides** are considered **low** or moderately toxic. All chemicals have a half-life in the environment.
- **“Half-life”** is defined as **the amount of time it takes to biodegrade one-half of the original amount.** Herbicides are broken down by sunlight and microbial activity in the soil.
- All chemicals are assigned **Lethal Dose (LD-50) numerical values** through certain testing procedures. An **LD-50** is the dose or amount of pesticide that can kill **50 percent** of the test animals when eaten or absorbed through the skin. LD-50 is expressed in milligrams of chemical **per kilogram of body weight** of the test animal (**mg/kg**).